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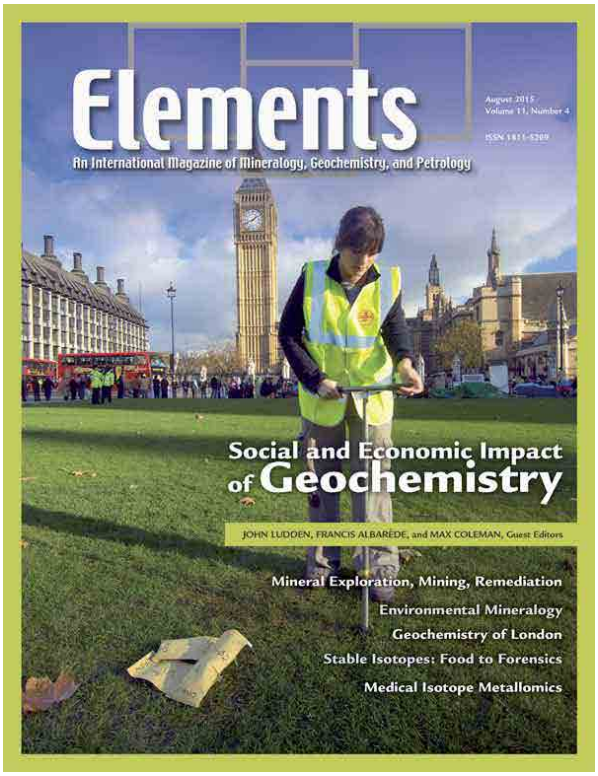
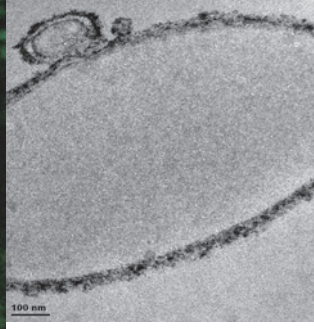


Environmental Mineralogy: New Challenges, New Materials



Cryo-transmission electron microscope image of a bacterial cell surface encrusted by UO_2 and budding a vesicle, after reduction of aqueous U(VI) to U(IV) by *Shewanella oneidensis* strain MR-1. Image from Shao et al. (2014)

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The close links between mineralogy and materials science are leading to major developments in how society deals more effectively with energy and environmental challenges. The fast expanding field of "environmental mineralogy" helps mitigate major environmental issues related to the impact of anthropic activities on the global ecosystem. Focusing on energy-related materials and environmental cleanup, this article shows how minerals inspire us to design new materials for advanced technologies needed for energy production, managing contaminated areas, and disposing of nuclear waste. We illustrate the environmental importance of nanomaterials, non- and poorly crystalline phases, and the interactions between minerals and ubiquitous microbial activity.

Keywords: energy materials, nuclear waste, contamination, heavy metals, uranium, biominerals

INTRODUCTION

Minerals are central to our natural and technological environments. They interact with the biosphere, buffer greenhouse gases (including CO_2), impact soil quality, remediate contaminated sites, and can be used to recycle or dispose of certain industrial wastes (such as nuclear waste). Minerals are also a source of naturally occurring pollutants, such as arsenic, as a result of the breakdown of primary As-containing minerals, e.g. arsenious pyrite and arsenopyrite. On the other hand, trapping pollutants in low-solubility phases and at mineral–water interfaces efficiently isolates toxic components, which can be found contaminating industrial/mining sites (Brown and Calas 2012). Furthermore, it is now universally recognized that minerals play a key role in low-temperature geochemical processes involving living organisms.

Environmental mineralogy is a fast-growing multidisciplinary field, addressing major societal concerns about the impact of anthropic activities on the global ecosystem. This has fostered developments in advanced analytical and theoretical tools, including large user facilities, specialized laboratory instruments, and numerical simulation methods to study the complex chemical and biological processes that impact the environment. The greater element selectivity, spatial resolution, and surface sensitivity provided by these instruments and methods have led to more robust environmental models.

A unified view of the environmental behavior of specific elements comes from determining their speciation in fluids, in minerals and on mineral surfaces and, more recently, at the biomineral interface. It is now recognized that the traditional boundaries between crystalline minerals, nanophases and nanoparticles, colloids and dissolved species are artificial, which challenges the current definition of a mineral (Caraballo et al. 2015). Environmentally important minerals include poorly to non-crystalline phases, as well as nanoscale materials. "Amorphous" solids, including glasses and gels, possess short-range order and the mineral–water interfaces present specific 2-D structures leading to unique chemical reactivities that have direct environmental and societal impacts (Brown and Calas 2012). As a consequence, geochemical reactions proceed along a continuum based on well-defined local structures and extending into less well-defined, poorly crystalline and amorphous materials.

In addition to being witnesses of and active agents in our environment, minerals inspire us to design innovative materials for energy conversion and energy storage devices, as well as for novel strategies to manage contaminated areas and toxic waste sites. The crossover between the materials science and mineralogical communities has resulted in new energy- and environmental-related technologies, based on mineral-inspired materials and leading-edge synthesis techniques.

This article illustrates how this new appreciation of minerals, combined with the beneficial exchange between (bio)mineralogical, materials, and environmental sciences, leads to new, socially beneficial, technologies and to new ways to mitigate the environmental impacts of anthropic activities.

MINERALOGY INSPIRES NEW MATERIALS AND TECHNOLOGIES

The approaches used by mineralogists to predict and characterize mineral structures and properties are shared with materials scientists so that mineralogy and the materials sciences have a symbiotic relationship. Crossover between the two fields has inspired new synthetic approaches and materials that are beneficially impacting society.

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For example, hydrothermal synthesis, which is widely used in experimental geology, produces high-quality quartz crystals for precision metrology used in satellite navigation, telecommunications, and global positioning. Synthetic cordierite ceramics, combining low thermal expansion coefficients with high refractoriness, good mechanical strength and open high porosity, are now used for catalytic converters that lower exhaust emissions in automobiles. Natural and synthetic zeolites, prepared using hydrothermal and sol–gel techniques originally developed for geochemical studies, are widely used in catalysis, in gas separation, and in ion exchange applications, which extend to medicine and chemical sensing. Similar sol–gel techniques are now a key method for producing nanoparticle powders, coatings, and composites, which include monolithic low-density phases, mesoporous solids, and inorganic–organic hybrid materials. Sol–gel production of rutile and anatase (both forms of TiO_2) permits control over their properties in pure and doped nanocrystals, leading to a wide variety of uses: in paints and sunscreens, as a photocatalyst for water splitting, for disinfection processes via reactions on the nanoparticle's surfaces, and for the development of light-to-energy conversion and storage.

New technological materials have also been developed as a result of high-pressure mineralogy experiments used to investigate deep planetary interiors (Brazhkin 2007). The laboratory synthesis of diamond and of boron nitride (cubic BN) has led to large-scale industrial production of these and other superhard, high-pressure phases. New technological applications have arisen from discovering that diamond can be deposited as thin films from the vapor phase and be synthesized from hydrothermal solutions, both having astrophysical and geochemical applications. The unique hardness, transparency, and chemical resistance of diamond make it the ideal material for diamond anvil cell experiments used to study minerals and other materials under extreme pressures. Perovskite-structured minerals, which dominate Earth's mantle, provide materials for technologies ranging from energy storage and conversion to communication science. Layered perovskites were the first high-temperature oxide superconductors; now, novel synthetic perovskites that contain organic cations and halide anions are being investigated as light-absorbing materials for photovoltaic applications (Grätzel 2014).

Recently discovered nitride spinels, γ-Si_3N_4 and γ-Ge_3N_4, synthesized in the stability domain of $(Mg,Fe)_2SiO_4$ ringwoodite, have a wide bandgap of several electron volts, meaning such semiconductor materials could be used for devices requiring higher voltage, frequency and temperature operating conditions and could lead to new optoelectronic materials. Other new nitrides with mineral-related structures have also been discovered using high-pressure synthesis (Salamat et al 2013).

These and many other examples highlight the significant crossover between materials technology and mineralogical research that continues to benefit both fields of study and to have positive environmental and societal impacts.

CARBON NANOMATERIALS: FROM PLANETARY ATMOSPHERES TO NEW ENERGY DEVICES

Graphitic carbon is a widespread and well-known mineral and geomaterial that plays a significant role in determining society's energy and environmental agenda through its use in sorption, catalysis, and battery and fuel cell technology. The 2-D crystal graphene is a single graphite sheet that has remarkable physical properties that are being developed for nanotechnology applications (Lazzeri and Barreiro 2014).

Incorporating nitrogen within graphitic sheets provides chemically reactive sites and allows control over the resulting electronic properties. These new carbon nitrides are also being studied in relation to the complex organic aerosols, or "tholins," produced in the upper atmosphere of Saturn's moon Titan and that contribute to its characteristic reddish haze (Fig. 1A, B). These carbon nitride semiconductors provide redox catalysts that are being developed for sustainable chemical processing (Thomas et al. 2008). Related amorphous to nanocrystalline $C_xN_yH_z$ polymers contain rings of heptazine (C_6N_7) and/or triazine (C_3N_3) linked via –N= and –NH– groups into graphene-like sheets (Fig. 1C, D) that absorb light and that can generate H_2 through photocatalysis of water or methanol (Wang et al. 2009) (Fig. 1E, F). Carbon nitrides can also reversibly intercalate Li^+ between or within the graphitic layers, potentially leading to Li-ion battery electrodes with improved storage capacity (Veith et al. 2013). Nitrogen-rich carbon nanomaterials also appear to offer protection to metal nanoparticle catalysts used in hydrogen- or methanol-burning fuel cells: the N-doped materials retain a higher catalytically active surface area after exposure to many (>500) operational cycles compared with pure carbon supports (Mansor et al. 2014). Attention is now being paid to carbon nitrides of one or just a few layers, analogous to

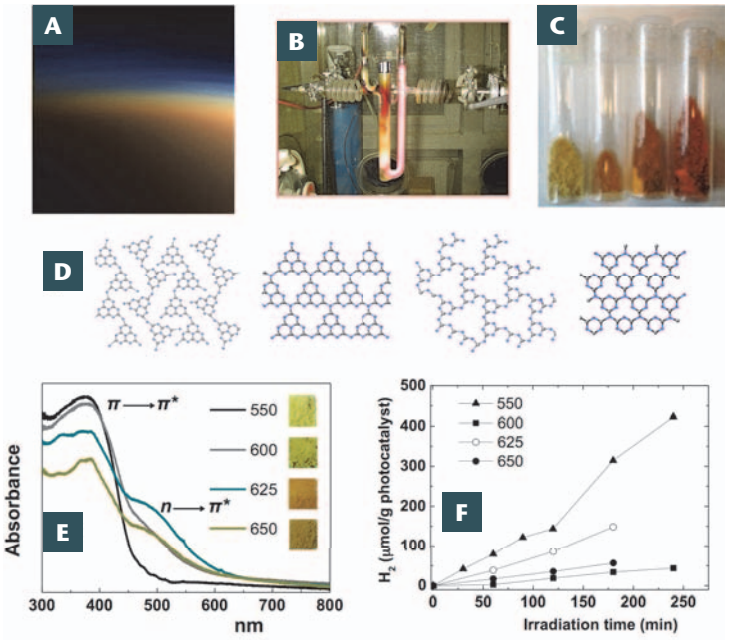

Figure 1 (**A**) Natural color image showing Titan's upper atmospheric haze associated with the presence of suspended aerosols. Photo courtesy of NASA/JPL-Caltech (**B**) A laboratory experiment forming tholins (carbon nitride polymers) to mimic production of Titan's atmospheric aerosols from methane and NH_3 precursors under irradiation (Quirico et al 2008). (**C**) Samples of graphitic carbon nitride (gCN) produced in the laboratory from different chemical precursors exhibiting varying degrees of condensation within the C–N layers resulting in different electronic and optical absorption properties. These materials are related to the aerosols used to model Titan's tholins. Graphitic carbon nitrides are being developed as new materials for reversible Li^+ uptake as battery anodes for energy storage applications, photocatalysis for solar energy harvesting and conversion, and as fuel cell catalyst supports (Wang et al 2009; Mansor et al 2014). (**D**) Structural motifs found among gCN materials are based on heptazine or triazine rings linked by –N= or –NH– units with different states of polymerization within the layers that leads to tuning the electronic and surface chemical properties. (**E**) UV-visible absorption spectra of gCN materials as a function of synthesis temperature and layer condensation. (**F**) Rate of H_2 evolution with gCN photocatalysts exposed to UV-visible radiation using methanol as a sacrificial agent (Jorge et al 2013).

graphene but with semiconducting properties and higher surface chemical reactivities (Algara-Siller et al. 2014). Along with conductive "inks" produced from C-graphene and nanotubes in various solvents, layered carbon nitride materials will produce new families of paintable electrodes and photochemically active surface coatings. The interplay between geochemical and materials science studies of these remarkable carbon-based nanomaterials is leading to new developments in nanotechnology with implications for energy sustainability and the environment.

GLASS TO GEL TRANSFORMATION AND THE IMMOBILIZATION OF NUCLEAR WASTE PRODUCTS

The radioactive waste that is generated by nuclear power reactors raises complex scientific and societal issues. The main long-term risk is contamination of the biosphere by long-lived radionuclides released after groundwater alteration of spent nuclear fuel (SNF). Over the short term, SNF is usually stored at reactor sites. But long-term geological disposal of SNF involves the use of many types of materials and processes, all with a time-dependence related to the changing composition of SNF over time—a result of the limited half-lives of the fission products and the long half-life actinides that will dominate over the long term. During storage in a geological repository, SNF physical and chemical properties may be modified over time, as a result of radionuclide decay (Ewing 2015). In countries such as France, Russia, Japan, India, and China, SNF is reprocessed, and high-level radioactive waste containing fission and activation products and minor actinides (Am, Np, Cm) is ultimately vitrified in a borosilicate glass (Grambow 2006). Under conditions relevant to a geological disposal environment, the reactions encountered during glass alteration by water include ion diffusion, hydrolysis of the glass structure, formation of a low-porosity gel by sparingly soluble species (mainly Si, Al, Ca), and precipitation of various mineral phases (e.g. smectite-type clays, rare earth element phosphates, zeolites) (Gin et al. 2015). The processes governing the corrosion of nuclear waste glasses and the formation of an alteration layer at the glass–water interface have been debated for several decades. Contrasting observations can result from different experimental conditions, including pH and composition of the alteration solution, temperature, or glass composition. For example, in closed systems, the glass alteration rate drops by 4 orders of magnitude due to development of a protective layer. In contrast, under open-system conditions, the activity of glass components remains low in the alteration solution, resulting in a high corrosion rate.

The structural relationships among glass components are consistent with the Pauling's rules observed in minerals and they govern glass stability and chemical durability (Calas et al. 2014). Spectroscopic investigation of the glass–solution interface during alteration has provided a molecular-scale description of the processes operating at the interface and revealed dramatic variations in the local structure of the pristine glass and alteration layer (Fig. 2; Pèlegrin et al. 2010). During alteration of a non-radioactive nuclear glass (SON68, the inactive equivalent of the technological R7T7 French nuclear glass) in deionized water at 90°C, the drastic structural modification of the local environment of Zr, used as a molecular-scale probe of glass structure, indicates that a dissolution–precipitation process has occurred as a result of the hydrolysis of the silicate framework (Fig. 2A). This may explain the observation by transmission electron microscopy of a sharp compositional and structural interface between pristine glass and the glass alteration layer during glass alteration in deionized water (Hellman et al. 2015). However, during alteration under near-saturation conditions with respect to the glass at pH 9, the local structure of the glass is retained, illustrating an in situ condensation process (Pèlegrin et al. 2010). This results in lower leaching rates and higher glass durability in the short term. The absence of hydrolysis under these pH conditions is consistent with recent experimental data on glass alteration (Gin et al. 2015). In contrast to Zr(IV), cations such as Fe(III) or Al(III) do not participate in the preservation of the silicate framework building the alteration layer (Fig. 2B). A major question remains concerning the compositional dependence of both the initial alteration rate and the residual corrosion rate

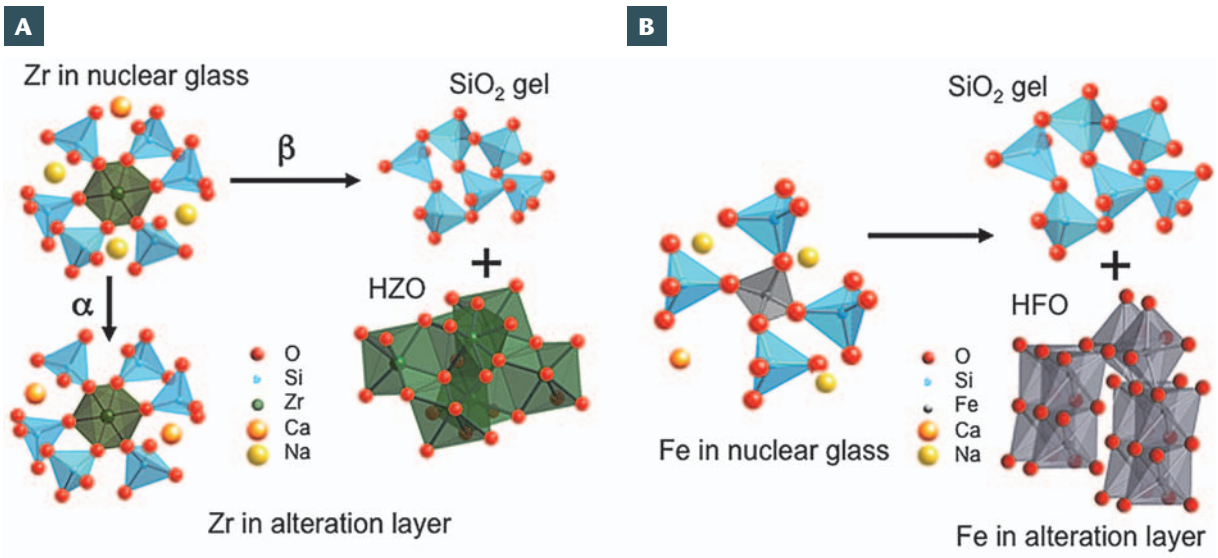

Figure 2 Modification of the local structure around Zr (**A**) and Fe (**B**), which are used as structural probes during the alteration of an inactive borosilicate nuclear glass, SON68. (**A**) In the pristine nuclear glass, octahedral Zr (green atoms) is in a networking position in the glass network, with well-defined Zr–O–Si linkages. During glass alteration under silica-saturated conditions (α), the local structure around Zr(IV) is retained in the alteration layer, a direct illustration of an in situ condensation process. During alteration in deionized water (β), the Zr–O–Si linkages disappear. Hydrous zirconium oxides (HZO) clusters (7-coordinated Zr) and silica gel domains coexist in the alteration layer, as a result of a dissolution–precipitation process. (**B**) In the pristine nuclear glass, tetrahedral Fe(III) (grey atoms) is a network-former. During alteration, either in silica-saturated conditions or in deionized water, Fe(III) converts to an octahedral coordination, leading to hydrous ferric oxides (HFO) coexisting with a silica gel in the alteration layer.

over the long term: the long-term stability of a nuclear-waste glass depends not only on the leaching processes at the glass–solution interface but also on the long-term stability of the alteration layers. New types of nuclear waste will be generated by the use of mixed oxide (plutonium/uranium) nuclear fuel (MOX) and other alternate nuclear fuels, and by future generations of nuclear reactors, such as the GEN IV. Understanding and predicting the long-term behavior of nuclear wastes, either through direct storage of SNF or the disposal of vitrified matrices resulting from spent fuel reprocessing, will require further research on the complex interactions between these man-made materials, the hydrosphere, and the biosphere.

MINERAL INTERACTIONS WITH THE BIOSPHERE: ENVIRONMENTAL APPLICATIONS

Microorganisms are known to affect the evolution of minerals, rocks, and ore bodies. They also act as biochemical "factories" for energy production and are useful in environmental waste management. Some microorganisms incorporate protein-based mechanisms for mediating redox reactions in their anaerobic metabolic cycles, leading to the production of methane or hydrogen. This property can now be industrially harnessed in biofilms to provide microbial fuel cells for environmentally sustainable energy production. Proteinaceous conducting "nanowires" extend from the surface of some bacteria and allow them to deliver electrons at distances up to several hundreds nm from the bacterial cell and so play a role in electrical transport and energy storage (Fig. 3A). The bacteria are also capable of catalyzing the reductive precipitation of toxic elements (Fig. 3B), including metal contaminants. Precipitates bound to extracellular polymeric substances (EPS) or membrane vesicles (Shao et al. 2014) improve survival rates of bacterial populations that are capable of detoxifying the cell environment at the same time as they immobilize toxic elements by producing solid (nanoscale) phases. The interplay between biology, geochemistry, materials science, and environmental science constitutes one of the frontier interfaces of modern science that impact on human welfare.

A main avenue by which microbial processes are being harnessed for applications is through environmental remediation. Contamination of the subsurface with toxic metals as a result of natural processes, mining, ore processing, and other industrial activities can be extensive, making conventional remediation approaches (i.e. excavation or pump-and-treat) impractical. However, stimulating the indigenous microbial community by the addition of a source of electrons (e.g. molasses), one can establish reducing conditions and promote the enzymatic or abiotic reduction of a redox-active metal. This application is particularly relevant in the case of uranium or chromium whose reduced forms are expected to be immobilized and to persist as an in situ waste. Bioremediation of sites contaminated with Cr(VI) has been attempted with amendments of organic matter that stimulate metal-reducing bacteria. The reduction of Fe(III) by *Shewanella alga* (strain BrY) results in aqueous Fe(II) that subsequently reduces Cr(VI) to Cr(III) and oxidizes Fe(II) back to Fe(III) (Hansel et al. 2003). The resulting Fe(III)–Cr(III) hydroxide [$Fe_{1-x}Cr_x(OH)_3 \cdot nH_2O$] is insoluble and effectively sequesters chromium. As Fe(III) reduction proceeds further, the fraction of Cr in the hydroxide increases, ultimately producing $Cr(OH)_3 \cdot nH_2O$, which is slightly more soluble but still represents a sink for Cr.

Bacteria in the genus *Shewanella* have the unusual ability to transfer electrons via extracellular electron transfer (EET), which enables them to carry out the remarkable feat of respiration using solid mineral phases. From an environmental perspective, *Shewanella* catalyzes the reduction of Fe(III) oxy/hydroxides and causes their transformation to magnetite or other Fe(II)-bearing minerals; biologically produced magnetite can then impact the mobility of metal/metalloid contaminants in the subsurface. This can be illustrated by the oxidation of the more toxic As(III) form of arsenic to the less toxic As(V) by biogenic magnetite resulting from the reduction of lepidocrocite by *Shewanella putrefaciens* (Ona-Nguema et al. 2010). Arsenic oxidation results from a reaction initially involving Fe(II) oxidation by molecular oxygen, which leads to the formation of hydroxyl radicals or other highly effective oxidants (e.g. $\bullet O_2^-$ and H_2O_2). These can then oxidize As(III) to

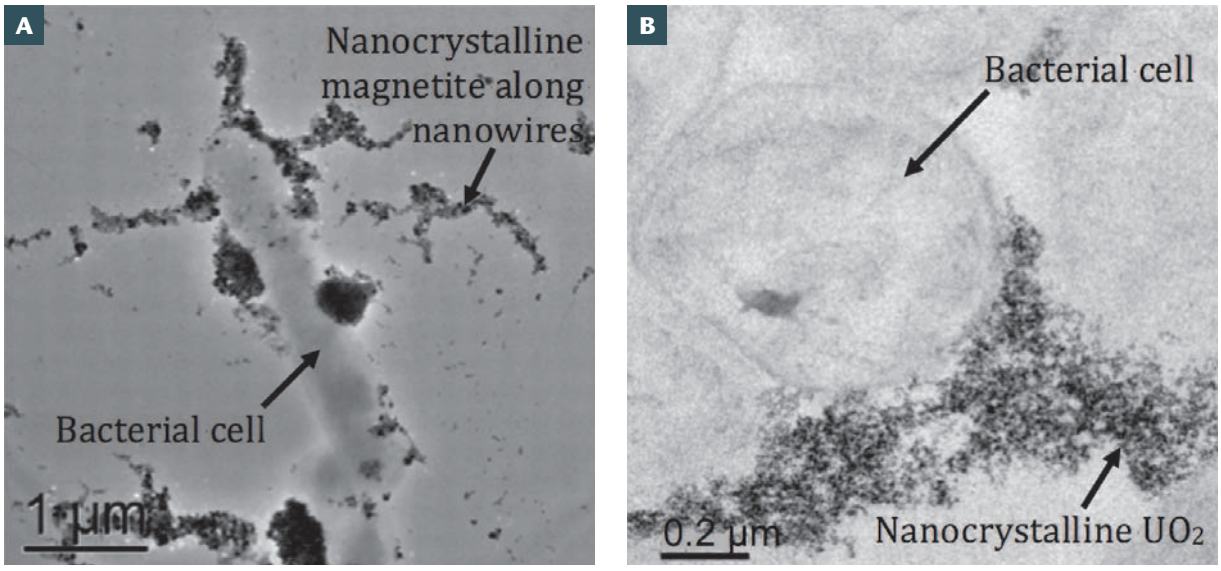

Figure 3 (**A**) Transmission electron microscope (TEM) images of whole mounts of *Shewanella oneidensis* MR-1 bacterial cells incubated in an aqueous suspension of silica hydrous ferric oxide. Nanocrystalline magnetite precipitates along extracellular features (i.e., nanowires) due to electron transfer facilitated by the bacteria. Image courtesy of Gorby et al. (2006). (**B**) TEM image of thin section of *Shewanella oneidensis* MR-1 with nanocrystalline UO_2 precipitates resulting from the reduction of aqueous U(VI) by the bacterium.

As(V) which can in turn adsorb onto the iron (hydr)oxides produced during the oxidation reaction. There are many examples of *Shewanella* and other metal-reducing bacteria impacting on the mobility of metal contaminants in ways that are beneficial to the environment.

Microorganisms, such as bacteria, are, of course, already present at highly contaminated sites, often bound to mineral surfaces by extracellular polymeric substances in the form of biofilms, and they can play an important role in the speciation of contaminants. Bacterially mediated biomineralization of a contaminated area may result from local modification of chemical conditions (e.g. pH, redox) or from passive mineral precipitation in the presence of organic matter. Acid mine drainage provides examples of bacterial mitigation of inorganic pollutants. For example, spatial and seasonal variation in microbial communities correlates with distinct trapping of arsenic by different bacterial strains. Fe-oxidizing bacteria and As-oxidizing bacteria promote the precipitation of Fe- and As-containing mineral phases, mostly in association with extracellular polymeric substances (Benzerara et al. 2011).

In the nuclear fuel cycle, the legacy of waste from uranium mining, milling, and processing has led to concerns about potential contamination in densely populated areas unless improved storage methods are developed. The type of reducing environments that are encountered in organic-rich soils, including peat horizons, preferentially concentrate uranium. Microbial reduction of U(VI) results in two potential products (Bernier-Latmani et al. 2010). One of these is uraninite, as 5 nm-size particles that effectively immobilize U(IV) and are relatively resistant to re-oxidation. The second is an insoluble "noncrystalline U(IV) phase" associated with bacterial biomass, the structure of which remains ill-defined. This latter product can occur in laboratory sediment columns, alpine meadows, or wetlands (Wang et al. 2013). Its continued presence in sediments post-remediation results from the cooperative action of sulfate- and metal-reducing bacteria (Bargar et al. 2013). The "non-crystalline U(IV) phase" is more labile than UO_2 (Cerrato et al. 2013) but represents, in most cases, a net uranium sink under reducing conditions. However, there is evidence that uranium can also associate with iron-rich organic-matter colloids of microbial origin, forming suspensions of mobile U(IV)-bearing particles (Wang et al. 2013). The string-shaped organic matter in these colloids includes iron-bearing nanoparticles (Fig. 4), as well as uranium. These species defy the common notion that U(IV) is always an immobile phase in the environment.

By directing electrons away from the bacterial cell, *Shewanella* and other species produce electrical currents that can be exploited in man-made microbial fuel cells. These devices harness the electrons produced by the oxidation of organic matter to generate electricity for a wide range of applications. Although the level of electrical current is low, microbial fuel cells can be used to power deep-water sensors, measure biological oxygen demand, or produce hydrogen from wastewater and other biomass resources (Ge et al. 2014). Furthermore, newly described urine-powered microbial fuel cells could represent a new technology for sending distress signals (Winfield et al. 2015).

The mechanisms of electron transfer tens of microns away from the cell surface include the production of long nanowires that represent extensions of the outer membrane and periplasm (Pirbadian et al. 2014). These structures include multiheme cytochromes that are responsible for extracellular electron transfer and suggest future possibilities for bionanotechnology to construct biological nanowires.

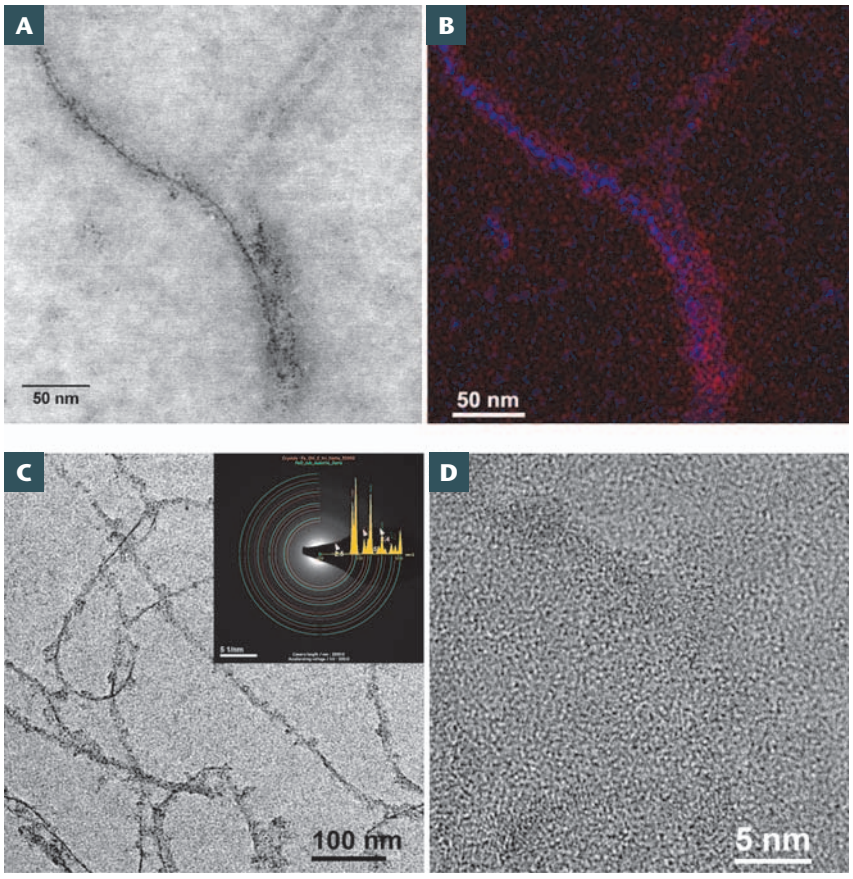

Figure 4 Transmission electron microscope (TEM) observations of U-bearing colloids in porewaters. (**A**) Scanning TEM image of U-bearing colloids in porewater. (**B**) The corresponding iron (Fe, blue) and carbon (C, red) energy dispersive X-ray spectroscopy (EDS) map of Figure 4A. (**C**) TEM image of U-colloids from the same sample as A and B; INSET: corresponding selected area electron diffraction pattern interpreted as a combination of trigonal $Fe(OH)_2$ and cubic FeO phases. (**D**) High-resolution TEM image of small U-bearing crystallites. Point EDS analyses on similar colloids show low, but statistically relevant, U concentrations in association with Fe and C (Wang et al. 2013).

CONCLUDING REMARKS

Minerals are key players in the environmental and technological issues that are important to modern society, especially when considering the importance of new "phases" such as gels and nanomaterials and the omnipresent reactivity of mineral–water interfaces, because such materials are now, or have the potential to become, exceptionally useful. Biological activity leads to the formation or alteration of mineral phases in nearly all environmentally relevant situations. Mineral–microbe interactions are being harnessed and developed for new energy technologies and for environmental cleanups. Mineralogical research has led the way in developing new approaches for materials synthesis and for in situ characterization techniques, while, at the same time, inspiring innovative materials based on structure–property relationships. In return, advances in materials research impact on environmental studies and widen our knowledge of mineral behavior. This symbiotic relationship is both healthy and necessary for our science and our students, who acquire experience and flair for mastering complex systems and problems in the Earth and environmental sciences.

Nevertheless, it remains for us to formalize and develop the links between microscopic properties, such as molecular/elemental speciation or surface reactivity, and macroscopic outcomes, such as element sequestration and sustainable energy production. Future challenges include developing the still largely unknown properties of nanoscale and poorly organized phases. Efficient environmental strategies and energy solutions will also depend on our ability to harness microorganisms and their activity. Developing field studies in partnership with advanced laboratory investigation and theoretical modeling will be necessary for maturing the new technologies that will be required for protecting and improving our environment.

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